

ORIGINAL ARTICLE

# Removal of Acid Red 33 from Aqueous Solution by Fenton and Photo Fenton Processes

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## KEYWORDS

Chemical oxygen demand (COD);  
Batch photo reactor;  
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Pseudo first order equation

**ABSTRACT:** In this project decolorization and mineralization of synthetic wastewater containing acid red 33 (AR33) was investigated by Fenton and photo Fenton processes in a batch photo reactor. A comparative assessment using Fenton and photo Fenton processes was performed after initial optimization studies such as varying pH, the concentration of pollutant, peroxide and iron. The color removal and mineralization efficiency of AR33 were calculated by Spectrophotometric and chemical oxygen demand (COD) tests. The degradation efficiency in photo Fenton process (98.5% in 10 min of reaction) was higher than Fenton ones (97.5% in 30 min). After 60 min of reaction, the removal of COD in photo Fenton and Fenton processes was 71% and 37.5%, respectively. Therefore, photo Fenton was the most effective process in partial mineralization of AR33. Kinetic constants were evaluated using pseudo first order equations to obtain the rate constant, K.

## INTRODUCTION

The growth and development of numerous industries that use organic dyes is significant in the last decades. The amounts of wastewaters created from industries are continuously developing. These wastewaters are often highly colored and turbid without relating to the dye concentration. Moreover, many dyes and their degradation products are toxic to life. According to their highly polluting properties, the color removal and treatment of wastewater should be noticed [1]. There are three classic methods for treatment of industrial

wastewater, but they have higher operating costs, contain the secondary pollution and need longer reaction time, so using new methods without these problems is essential[2]. Advanced oxidation processes (AOPs) offer a highly reactive, nonspecific oxidant namely hydroxyl radical (OH<sup>•</sup>), that oxidize a broad range of pollutants quickly and non-selective in water and wastewater [3-5]. AOPs such as Fenton and photo-Fenton catalytic reactions [6], UV/ H<sub>2</sub>O<sub>2</sub> process [7] and semiconductor photo catalysis [8] have been studied

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under a wide range of experimental conditions in order to reduce the color and organic load of the wastewater. Fenton's reagent is a mixture of hydrogen peroxide and ferrous ion ( $\text{Fe}^{2+}$ ) which creates hydroxyl radicals, widely used for oxidation of organic pollutant and reduction of the chemical oxygen demand (COD) in water [9]. The Fenton and photo-Fenton (UV/Fenton) process could be used promptly as a hopeful and attractive treatment method for an effective decolorization and degradation of dyes in a textile wastewater [10]. The removal rate is strongly reliant on the initial concentration of the dye,  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  [11]. The main purpose of this study was to investigate the possibility of decolorization and mineralization of AR33 by Fenton and photo-Fenton processes. The effect of various operational parameters such as pH,

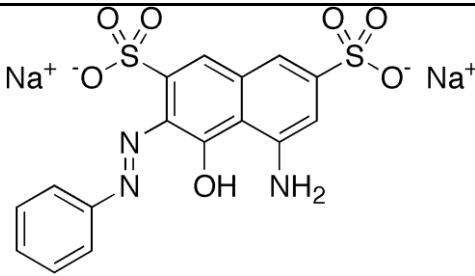
concentration of  $\text{H}_2\text{O}_2$ ,  $\text{Fe}^{2+}$  and AR33 was also examined on the effectiveness of Fenton and photo-Fenton reactions.

## MATERIALS AND METHODS

### Materials

Acid red 33 (AR33) was purchased from an Afrand Tuska company of Iran and used without further purification. The chemical properties of AR33 are presented in Table 1. Ferrous sulphate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) as the source of Fe (II), Hydrogen peroxide solution (30% w/w),  $\text{H}_2\text{SO}_4$  and NaOH are all supplied from Merck. Distilled water was used for the entire work.

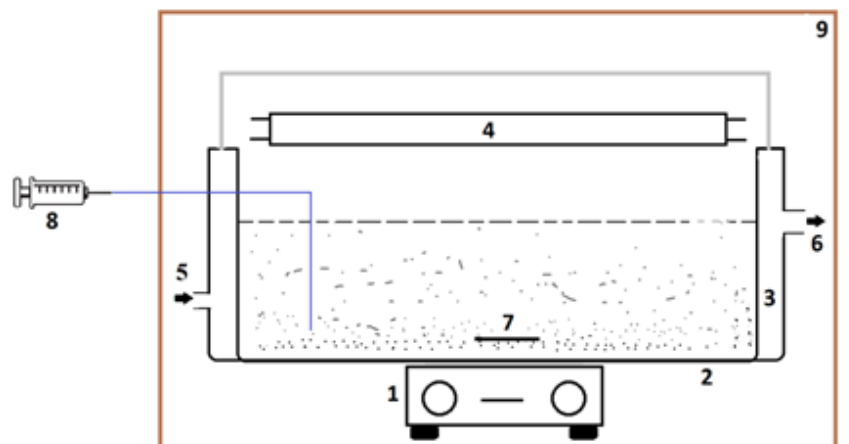
Table 1. Chemical structure and maximum absorption of AR33.

Pollutant	Molecular structure	$\lambda_{\text{max}}(\text{nm})$	Molecular Mass
Acid Red 33		526	467.39

### Photo reactor

In this project, experiments are performed in a batch reactor with a total volume of 1 L. The light source was a mercury lamp, Philips 15W (UV-C), which positioned horizontally above the reactor. The reactor is made of glass, covered with an aluminum sheet to prevent loss of UV light, and equipped with a sampling system (Figure 1). The temperature remained fixed at 25 °C in all tests

by a water-flow exchanger, using an external circulating flow of a thermostatic bath (BW20G model from Korean Company). The solution in the reactor mixed well with magnetic stirrer. The initial pH of the solution was adjusted using a Basic pH Meter PT-10P Sartorius Instrument Germany Company.



**Figure 1.** Schematic diagram of laboratory-scale experimental set-up used.

1- Magnetic Stirrer, 2-Batch reactor, 3-Jacket water, 4- UV lamp,  
5- Cooling water supply from thermostat, 6- Cooling water return, 7- Magnetic bar, 8- Sampling port, 9-Dark box

### **Analytical Procedure**

Various concentrations of  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  are used for optimization in Fenton and photo Fenton processes. The reactions are quenched by adding 10% aqueous solution of sodium sulfite. The lamp was switched on to start the reaction in the photo Fenton process. The solution in the reactor was mixed by a stirrer to prevent from the settling of Iron ions and keeps the suspension to be homogenous. The pH was adjusted by adding NaOH or  $\text{H}_2\text{SO}_4$  (0.1 M) and studied in the range of 1 to 8.

Samples were taken, centrifuged and filtered, then analyzed by a UV-Vis spectrophotometer (Agilent, 5453, American) at 526 nm. The Calibration plot according to the Beer Lambert's law was applied by concerning the absorbance to the concentration. The decrease in the absorbance at 526 nm is due to the color removal of AR33 solution.

Hydrogen peroxide interferes with the Chemical oxygen demand (COD) and absorbance tests. Therefore, the samples are treated with  $\text{MnO}_2$  powder to decay residual amount of  $\text{H}_2\text{O}_2$  [12]. Before each examination, samples are centrifuged and filtered to remove  $\text{MnO}_2$  powder. The COD was determined through a HACH-5000

spectrophotometer via a dichromate solution as an oxidant in strong acidic conditions [13]. At the end of the reaction, the solution was settled and then it was filtered to remove the precipitated. A sample was diluted with distillate water, then 1.5 ml of potassium dichromate and 3.5 ml of sulfuric acid as two reagents were mixed with 2.5 ml of the sample in a test tube. The sample was digested into the COD reactor for 2 h at about 150 °C. After acidic digestion, the sample was cooled and measured by the COD meter to estimate the mineralization efficiency of AR33 [14].

## **RESULTS AND DISCUSSION**

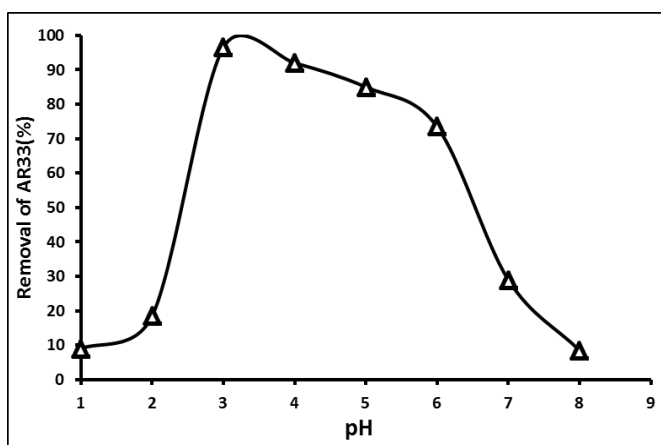
### **Effect of pH on Fenton and photo Fenton processes**

The pH value has a significant influence on the oxidation potential of hydroxyl radicals because there is a conjoint relation between them. Moreover, the concentration of inorganic carbon and Ferric ions are strongly affected by the pH value. Therefore, the effect of pH in the Fenton and photo Fenton reaction was investigated in the range of 1 to 8. The pH value affects

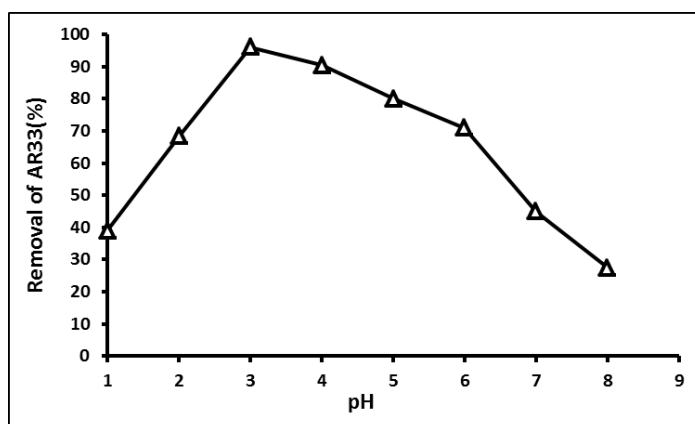
the production of  $\text{OH}^\cdot$  radicals and thus the oxidation efficiency. As it can be seen from Figure 2 and 3, with an increase in the pH of the solution from 1 to 3, the removal efficiency of AR33 was increased from 9% to 96.5% and 39% to 96% after 30 and 10 min of reaction in Fenton and photo-Fenton processes, respectively. However, the color removal efficiency decreased from 96.5% to 8.5% for Fenton system and from 96% to 27.5% in the photo-Fenton processes by enhancing the pH value from 3 to 8.

At a pH above 4, the color removal efficiency decreased sharply because iron starts to precipitate as  $\text{Fe}(\text{OH})_3$  and its ability to catalyze  $\text{H}_2\text{O}_2$  decreases and also the transmission of the radiation into the solution decreases

[15-16]. Furthermore, with increasing pH, the oxidation potential of hydroxyl radical was decreased and hydrogen peroxide could be unchanging at a pH below 2, perhaps it absorbs a proton and produces an Oxonium ion ( $\text{H}_3\text{O}^+$ ). It is possible that the reactivity with ferrous ion decreases with an Oxonium ion [17]. Thus, the number of hydroxyl radicals was decreased and the removal efficiency reduced. Another reason for the decrease in degradation efficiency at pH higher than 3 originates from the dissociation and auto-decomposition of hydrogen peroxide [18]. However, in the photo-Fenton process, the removal efficiency reached as high as 96% only at 10 min of reaction verifying the fact that UV light improved the removal efficiency of AR33.



**Figure 2.** Effect of pH on the removal efficiency of AR33 with Fenton process ( $[\text{AR33}]_0 = 250 \text{ mg/l}$ ,  $[\text{H}_2\text{O}_2]_0 = 15 \text{ mM}$ ,  $[\text{Fe}^{2+}] = 0.28 \text{ mM}$ , time=30 min).



**Figure 3.** Effect of pH on the removal efficiency of AR33 in photo Fenton process ( $[\text{AR33}]_0 = 250 \text{ mg/l}$ ,  $[\text{H}_2\text{O}_2]_0 = 16 \text{ mM}$ ,  $[\text{Fe}^{2+}] = 0.28 \text{ mM}$ , time=10 min).

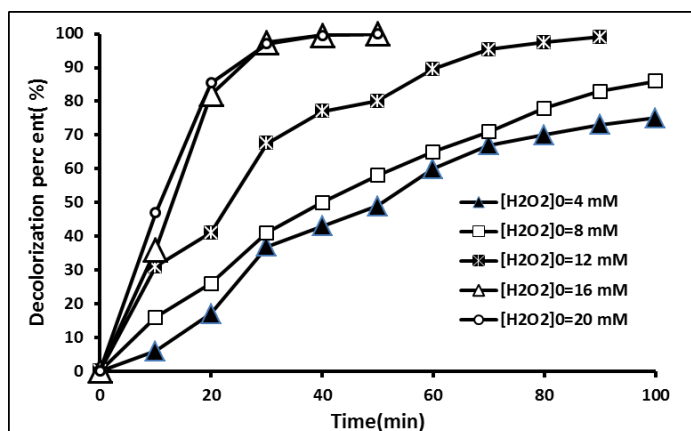
### Effect of initial concentration of hydrogen peroxide

The influence of initial hydrogen peroxide concentration on the color removal efficiency of AR33 is presented in Figures 4 and 5. Experiments were performed at a constant initial pH of 3 and changed  $\text{H}_2\text{O}_2$  from 4 to 20 mM and 8 to 24 mM within the irradiation time of 100 and 30 min for Fenton and photo Fenton process, respectively. After 30 min of reaction in Fenton process, when the dosage of  $\text{H}_2\text{O}_2$  was increased from 4 to 16 mM, the removal efficiency of AR33 enhanced from 37 to 97.5%. Because more  $\text{OH}^\bullet$  radicals were produced and degradation efficiency enhanced. However, above this limit the progress was not significant. In photo-Fenton process, with increasing the concentration of  $\text{H}_2\text{O}_2$  from 8 to 20 mM, the color removal efficiency, increased from 28 to 98.5%, but higher concentrations of hydrogen peroxide act as free-radical scavenger itself and increase in the degradation efficiency was not noticeable [19]. Besides, this trend may be according to

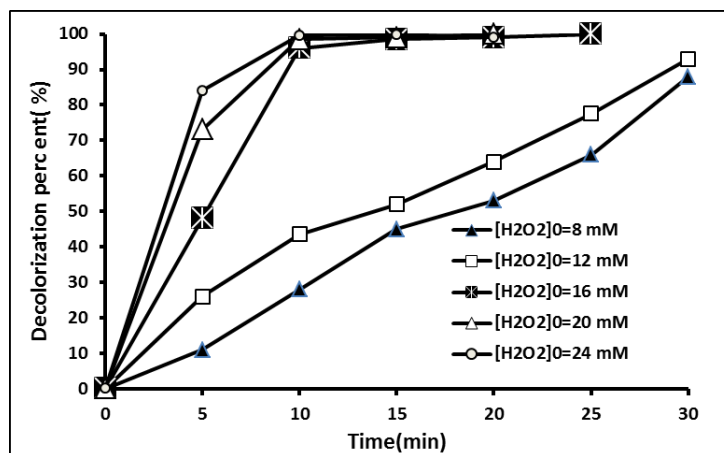
the auto disintegration of  $\text{H}_2\text{O}_2$  to water and oxygen and additional amount of  $\text{H}_2\text{O}_2$  will react with  $\text{OH}^\bullet$  radicals competing with AR33 molecules.

An optimum concentration of  $\text{H}_2\text{O}_2$  for Fenton and photo Fenton processes were 16 and 20 mM, respectively. Thus,  $\text{H}_2\text{O}_2$  should be added at an optimum concentration to obtain the best results. However, not all of the added hydrogen peroxide was spent. The low remaining concentration of  $\text{H}_2\text{O}_2$  is an important advantage of the photo Fenton relation to the Fenton process.

However, with an increase in the concentration of hydrogen peroxide from 20 to 24 mM, the color removal efficiency of AR33 was not considerable. Therefore, the dose of  $\text{H}_2\text{O}_2$  at 20 mM was considered as the optimal concentration for photo Fenton process due to the economic point of view.



**Figure 4.** The effect of the initial concentration of  $\text{H}_2\text{O}_2$  on Fenton process ( $[\text{AR33}]_0 = 250 \text{ mg/l}$ ,  $[\text{Fe}^{2+}]_0 = 0.28 \text{ mM}$ ,  $\text{pH} = 3$ ,  $\text{time} = 100 \text{ min}$ ).

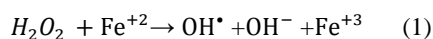


**Figure 5.** The effect of the initial concentration of H<sub>2</sub>O<sub>2</sub> on the photo Fenton process ([AR33]<sub>0</sub> = 250 mg/l, [Fe<sup>2+</sup>]<sub>0</sub> = 0.28 mM, pH = 3, time=30 min).

### Effect of initial concentration of Fe (II)

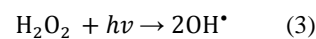
The concentration of ferrous ion is one of the key variables to influence the Fenton and photo-Fenton processes. In this project, various concentrations of Fe<sup>2+</sup> (from 0.15 to 0.4 mM) were used to achieve its optimum concentration.

As it is shown in Figure 6 and 7, the removal rate of AR33 increased with increasing the amounts of iron salt according to the following equations (Eqs. 1-2)

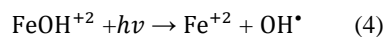


The maximum percent of color removal was 97.5% and 98.5% with 0.3 and 0.25 mM of Fe<sup>2+</sup> at 30 and 10 min in Fenton and photo Fenton processes, respectively. Especially for photo Fenton process, addition of iron salt above 0.25 mM did not affect the removal efficiency, considerably. This is owing to the fact that, at a Fe (II) concentration higher than the optimum, the initial

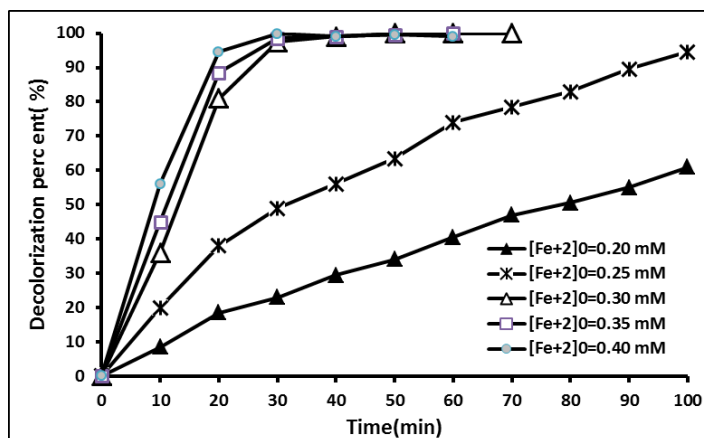
formation rate of hydroxyl radicals, mainly produced from the disintegration of H<sub>2</sub>O<sub>2</sub>, was so high that many of hydroxyl radicals were consumed by the side reactions before they could be utilized effectively for the removal of the AR33 (Eq. 3)[20].



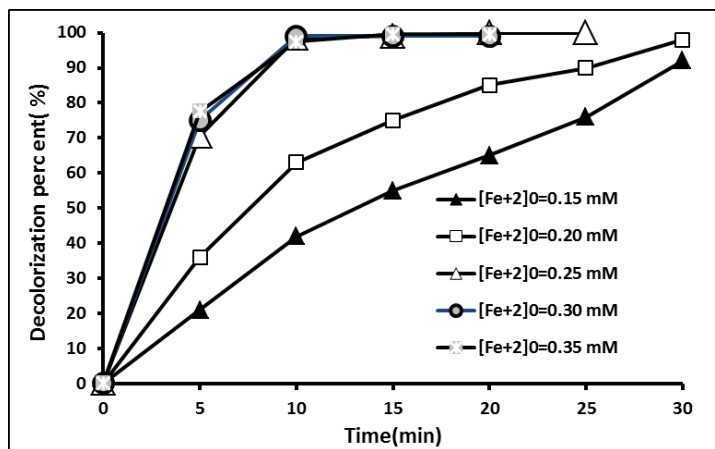
Furthermore, it was resulted in brown turbidity that hindered the absorption of the UV light necessary for photolysis and caused the recombination of OH radicals [21]. Additionally, the effect of the dosage of Ferrous ion in Fentone process is higher than photo-Fenton ones. This finding is in agreement with the researches of Liou et al., (Eq.4) [22].



After the Fenton and photo Fenton treatments, the residual iron was removed by raising the pH of the solution to the alkaline condition [23].



**Figure 6.** Effect of the initial concentration of Fe<sup>2+</sup> in Fenton process  
 ([AR33]<sub>0</sub> = 250 mg/l, [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> = 16 mM, pH= 3, time=100 min).



**Figure7.** Effect of the initial concentration of Fe<sup>2+</sup> in photo Fenton process  
 ([AR33]<sub>0</sub> = 250 mg/l, [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> = 20 mM, pH= 3).

**Effect of initial concentration of AR33**

The impact of the initial concentration of AR33 on the color removal efficiency was investigated and showed in Figs. 8 and 9. It was clear that for Fenton and photo-Fenton processes the removal efficiency decreases with enhancing the initial concentration of the AR33.

Increase of AR33 from 50 to 375 mg/l leads to decreases in the removal of color from 95.5% to 60.5% for Fenton and from 91.5% to 61% for photo-Fenton

process after 20 and 5 min of reaction, respectively. The number of dye molecules, was enhanced by an increase in dye concentration. Therefore, there was not enough hydroxyl radical and the removal rate reduced [24]. In photo-Fenton process, the permeation of photons entering into solution reduces at high dye concentration, thus the concentration of hydroxyl radical decreases [25].

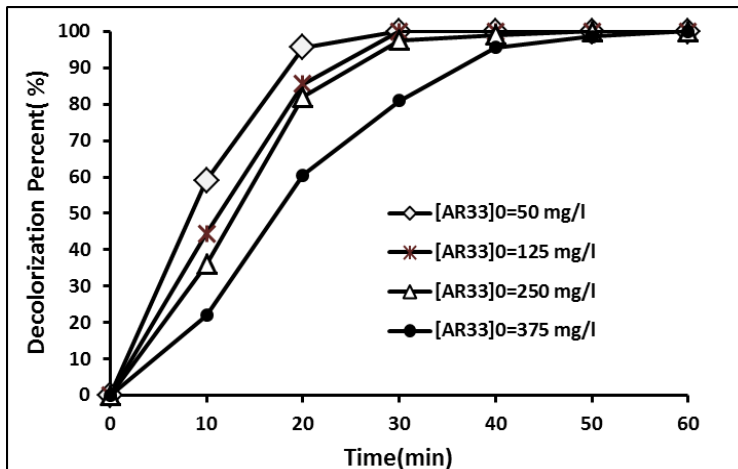


Figure 8. The influence of the initial concentration of AR33 in Fenton process ( $[H_2O_2]_0 = 16 \text{ mM}$ ,  $[Fe^{2+}]_0 = 0.3 \text{ mM}$ ,  $\text{pH} = 3$ ).

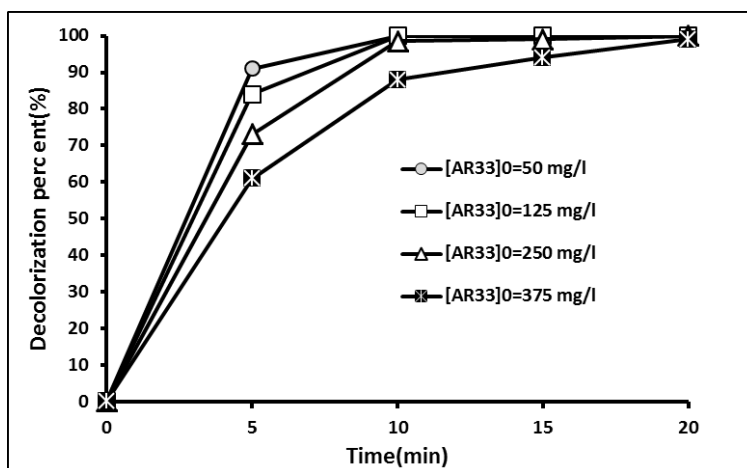


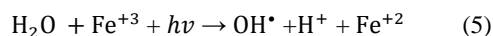
Figure 9. The effect of the initial concentration of AR33 in photo Fenton process ( $[H_2O_2]_0 = 20 \text{ mM}$ ,  $[Fe^{2+}]_0 = 0.25 \text{ mM}$ ,  $\text{pH} = 3$ ).

### Reduction of COD in Fenton and photo-Fenton processes

In the wastewater treatment, the intermediate products of some pollutants can sometimes be more toxic than the initial compound. The COD values have been concerned with the total concentration of organics in the solution and it is important to measure the COD after the degradation of the dye to prove the mineralization extent of the dye. Thus, reduction of COD is also investigated along with degradation of AR33. The removal

efficiency of COD in different processes is shown in Figures 10 and 11.

The removal of COD in photo Fenton process was more effective (71%) than Fenton process (37.5%) for 60 min of irradiation time. This can be described by the broad regeneration of all  $Fe^{3+}$  to  $Fe^{2+}$  enhanced by UV (Eq. 5) [26].





Fenton process is able to destroy AR33 effectively, but dye. pretty have difficulty with total mineralization of the

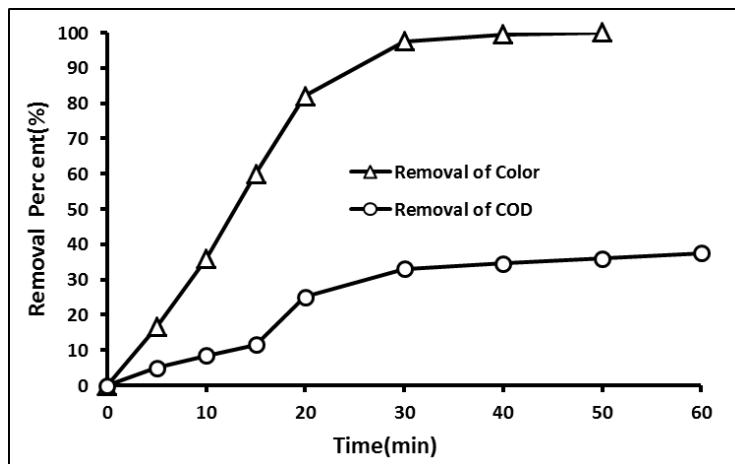


Figure 10. The removal of color and COD in Fenton process at optimum conditions ([AR33]<sub>0</sub> = 250 mg/L, ([H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> = 16 mM, [Fe<sup>2+</sup>]<sub>0</sub> = 0.3 mM, pH = 3).

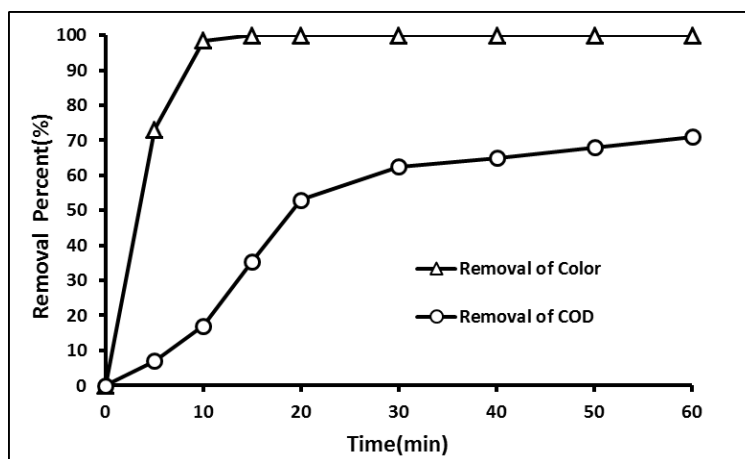


Figure 11. The removal of color and COD in photo-Fenton process at optimum conditions ([AR33]<sub>0</sub> = 250 mg/l, ([H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> = 20 mM, [Fe<sup>2+</sup>]<sub>0</sub> = 0.25 mM, pH = 3).

### Kinetic study for decolorization of AR33

The hydroxyl radical produces in Fenton and photo-Fenton processes and it is a main oxidizing agent for degradation of AR33.

Thus, the kinetics for AR33 degradation by Fenton and photo-assisted Fenton processes can be described as (Eq. 6):

$$\frac{-dC_{AR33}}{dt} = k_{AR33} C_{AR33} C_{OH\cdot} \quad (6)$$

Where  $C_{AR33}$  is the concentration of dye,  $C_{OH\cdot}$  is the hydroxyl radical concentration and  $k_{AR33}$  is the second-order rate constant. The second-order rate equation can be used to fit the experimental data. In this study the concentration of hydroxyl radicals is higher than that of AR33, so hydroxyl radicals were in excess related to the concentration of AR33 and the Eq. 6 can be converted to a pseudo-first-order rate equation;

$$\frac{-dC_{AR33}}{dt} = k_{ap}C_{AR33} \quad (7)$$

The  $k_{ap}$  is the pseudo-first-order rate constant. This method is in agreement with similar studies by several researchers [27-28]. By integrating from the Eq. 7, the following equation (Eq. 8) was obtained.

$$\ln\left(\frac{[AR33]_0}{[AR33]_t}\right) = K_{app} \times t \quad (8)$$

Where  $[AR33]_0$  and  $[AR33]_t$  are the concentration of

AR33 at times 0 and  $t$ ,  $K_{app}$  is a pseudo-first-order rate constant and  $t$  is the time in minutes. After linear regression analysis, the first order rate constants and half-life of reaction were determined (Table 2) [29].

Figure 12A and B, approve the important accelerating effect of photo Fenton reactions on the degradation of AR33 in comparison with Fenton process. Almost both of the processes followed the pseudo first order kinetics because in both of them  $R^2$  is near 1.

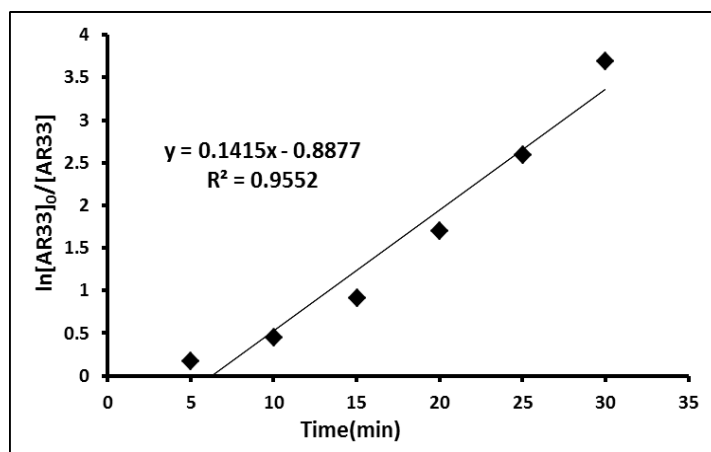


Figure 12. A) Kinetic fit for degradation of AR33 in Fenton process at optimum conditions ( $[AR33]_0 = 250$  mg/L,  $[H_2O_2]_0 = 16$  mM,  $[Fe^{2+}]_0 = 0.3$  mM, pH = 3).

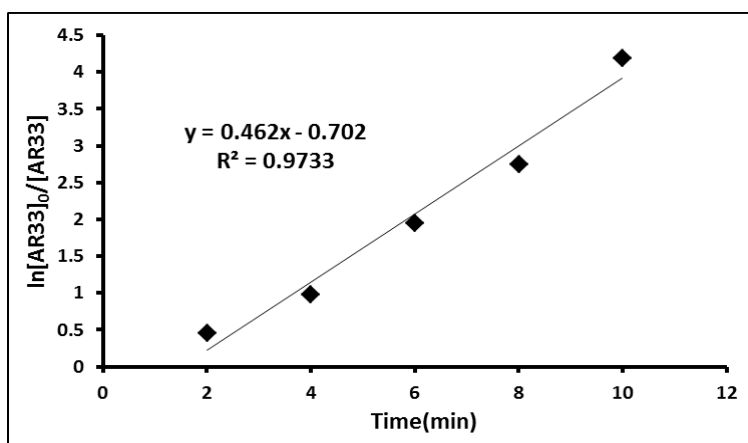


Figure 12. B) Kinetic fit for degradation of AR33 in photo Fenton process at optimum conditions ( $[AR33]_0 = 250$  mg/l,  $[H_2O_2]_0 = 20$  mM,  $[Fe^{2+}]_0 = 0.25$  mM, pH = 3).

**Table 2.** Rate constant and half-life of different processes for the removal of AR33 in optimum conditions.

S. no	Process	K, min <sup>-1</sup>	t <sub>1/2</sub> , min	R <sup>2</sup>
1	Fenton	1.415×10 <sup>-1</sup>	4.9	0.9552
2	Photo Fenton	4.62×10 <sup>-1</sup>	1.5	0.9733

## CONCLUSIONS

The resulting conclusions could be reached by using Fenton and Photo-Fenton processes;

-The color removal efficiency of AR33 was influenced by the initial concentration of the dye, Fe<sup>2+</sup>, H<sub>2</sub>O<sub>2</sub>, and pH. The best conditions for the removal of AR33 in Fenton process were obtained at pH = 3.0, the initial Fe<sup>2+</sup> concentration of 0.3 mM and an initial H<sub>2</sub>O<sub>2</sub> dosage at 16 mM with a dye concentration of 250 mg/l.

-In the photo Fenton process, the optimum conditions for degradation of dye were pH 3, initial concentration of Fe<sup>2+</sup> at 0.25 mM and 20 mM of hydrogen peroxide for an initial AR33 at 250 mg/l. The low concentration of Fe<sup>2+</sup> had more positive effect for degradation than higher ones.

-The removal of COD in Fenton process was relatively low (37.5% in 60 min) and it can be an effective pretreatment technique before biological method.

-The setup of the reactor was simple and no harmful chemical component was applied in these methods. Both of Fenton and photo-Fenton processes were influential methods for decolorization of AR33, but photo-Fenton process was the most helpful for the removal of COD (71%). The difference between them was little for the color removal of AR33, so in the color removal study the Fenton method is more suitable than the photo Fenton from an economic point of view.

## ACKNOWLEDGEMENTS

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## REFERENCES

- Panakoulias T., Kalatzis P., Kalderis D., Katsaounis A., 2010. Electrochemical degradation of reactive Red 120 using DSA and BDD anodes. *J Appl Electrochem.* 40, 1759–1765.
- Yahiat S., Fourcade F., Brosillon S., Amrane A., 2011. Photocatalysis as a pre-treatment prior to a biological degradation of cyproconazole. *Desalination.* 281, 61–67.
- Moradi H., Sharifnia S., Rahimpour F., 2015. Photocatalytic decolorization of reactive yellow 84 from aqueous solutions using ZnO nanoparticles supported on mineral LECA. *Mater Chem Phys.* 158, 38–44.
- Behnajady M.A., Modirshahla N., Fathi H., 2006. Kinetics of decolorization of an azo dye in UV alone and UV/H<sub>2</sub>O<sub>2</sub> processes. *J Hazard Mater B.* 136, 816–821.
- Shokri A., 2015. Degradation of 2-Nitrophenol from Petrochemical Wastewater by Ozone. *Russ J Appl Chem.* 88, 2038–2043.
- Katsumata H., Kawabe S., Kaneco S., Suzuki T., Ohta K., 2004. Degradation of bisphenol A in water by the photo-Fenton reaction. *J Photochem Photobiol A: Chem.* 162, 297–305.
- Malik P.K., Sanyal S.K., 2004. Kinetics of decolourisation of azo dyes in wastewater by UV/H<sub>2</sub>O<sub>2</sub> process. *Sep Purif Technol.* 36, 167–175.

8. Shokri A., Mahanpoor K., Soodbar D., 2016. Degradation of 2-Nitrophenol from Petrochemical Wastewater by UV/NiFe<sub>2</sub>O<sub>4</sub>/Clinoptilolite process. *Fresenius Environ Bull.* 25, 500-508.
9. Momani F.A., Sans C., Esplugas S., 2004. A comparative study of the advanced oxidation of 2,4-dichlorophenol. *J Hazard Mater B.* 107, 123-9.
10. Kang S.F., Liao C.H., Po S.T., 2000. Decolorization of textile wastewater by photo-Fenton oxidation technolog. *Chemosphere.* 41, 1287-94.
11. Malik P.K., Saha S.K., 2003. Oxidation of direct dyes with hydrogen peroxide using ferrous ion catalys. *Sep Purif Technol.* 31, 241-50.
12. El-sousy K., Hussien A., Hartani K., El-Aila H., 2007. Elimination of Organic Pollutants using Supported Catalysts with Hydrogen Peroxide. *Jordan J Chem.* 2, 97-103.
13. Kolthof I.M., Sandell E.B., Meehan E.J., Buckstein S., *Quantitative Chemical Analysis*, 4th ed., Macmillan, New York, 1862-1867.
14. Badawy M.I., 2006. Advanced oxidation processes for the removal of Organophosphorus pesticides from wastewater. *Desalination.* 194, 166-175.
15. Ming-Chun L., Jong-Nan C., Cheu-Ping C., 1999. Oxidation of dichloros with H<sub>2</sub>O<sub>2</sub> using ferrous ion as catalyst. *J Hazard Mater.* 65, 277-288.
16. Tunc S., Gurkan T., Duman O., 2012. On-line spectrophotometric method for the determination of optimum operation parameters on the decolorization of Acid Red 66 and Direct Blue 71 from aqueous solution by Fenton process. *Chem Eng J.* 181-182, 431-442.
17. Zhao X.K., Yang G.P., Wang Y.J., Gao X.C., 2004. Photochemical degradation of dimethyl phthalate by Fenton reagent. *J Photochem Photobiol A Chemistry.* 161, 215-20.
18. Romero V., Acevedo S., Marco P., Gimenez J., Esplugas S., 2016. Enhancement of Fenton and photo-Fenton processes at initial Circumneutral pH for the degradation of the  $\beta$ -blocker metoprolol. *Water Res.* 88, 449-457.
19. Schrank S.G., Jose H.J., Moreira R.F.P.M., Schroder H.F., 2005. Applicability of Fenton and H<sub>2</sub>O<sub>2</sub>/UV reactions in the treatment of tannery wastewaters. *Chemosphere.* 60, 644-655.
20. Catalkaya E.C., Sengul F., 2005. Application of Box-Wilson experimental design method for the photo degradation of bakery's yeast industry with UV/H<sub>2</sub>O<sub>2</sub> and UV/H<sub>2</sub>O<sub>2</sub>/Fe (II) process. *J Hazard Mater.* 128, 201-207.
21. Wailling C., 1975. Fenton's reagent revisited. *Acc Chem Res.* 8, 125-131.
22. Lioua M.J., Lub M.C., Chena J.N., 2003. Oxidation of explosives by Fenton and photo-Fenton processes. *Water Res.* 37, 3172-3179.
23. Zhao X.K., Yang G.P., Wang Y.J., Gao X.C., 2004. Photochemical degradation of dimethyl phthalate by Fenton reagent. *J Photochem Photobiol A Chemistry.* 161, 215-20.
24. Ramirez J.H., Duarte F.M., Martins F.G., Costa C.A., Madeira L.M., 2009. Modelling of the synthetic dye Orange II degradation using Fenton's reagent: from batch to continuous reactor operation. *Chem Eng J.* 148, 394-404.
25. Daneshvar N., Rabbani M., Modirshahla N., Behnajady M.A., 2005. Photo oxidative degradation of Acid Red 27 in a tubular continuous-flow photo reactor: influence of operational parameters and mineralization products. *J Hazard Mater.* 118, 155-60.
26. Bali U., Catalkaya E.C., Sengul F., 2003. Photochemical degradation and mineralization of phenol: A comparative study. *J Environ Sci Health: Part A.* 38, 2259-2275.
27. Javier Benitez F., Beltran-Heredia J., Acero J. L., Javier Rubio F., 2000. Rubio contribution of free radicals to Chlorophenols decomposition by several advanced oxidation processes. *Chemosphere.* 41, 1271-1277.

28. Shokri A., Mahanpoor K., Soodbar D., 2015. Degradation of Ortho-Toluidine in petrochemical wastewater by Ozonation, UV/O<sub>3</sub>, O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> and UV/O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> processes. Des Water Treat. 2015, 1-10.

29. Bayarri B., Gimenez J., Curco D., Esplugas S., 2005. Photocatalytic degradation of 2, 4-dichlorophenol by TiO<sub>2</sub>/UV: kinetics, actinometries and models. Catal Today. 101, 227–236.

